

# Electrical characterization of amorphous lanthanum aluminate thin films grown by molecular-beam deposition on silicon

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Amorphous  $\text{LaAlO}_3$  thin films were deposited at room temperature directly on  $n$ -type and  $p$ -type Si (001) by molecular beam deposition. The dielectric properties of the stoichiometric amorphous  $\text{LaAlO}_3$  thin films deposited on silicon were determined through capacitance-voltage and current-voltage measurements. The electrical measurements indicate that the amorphous  $\text{LaAlO}_3$  thin films have a dielectric constant ( $K$ ) of  $K=16\pm2$ . This is significantly lower than the  $K=24$  of crystalline  $\text{LaAlO}_3$ . The equivalent oxide thickness values range between 9.8 and 15.5 Å for films deposited on  $n$ -type silicon with physical thicknesses of 45–75 Å. © 2006 American Institute of Physics. [DOI: 10.1063/1.2182019]

The scaling of  $\text{SiO}_2$  in metal-oxide-semiconductor field-effect transistors (MOSFETs) is approaching its fundamental limit, which has been estimated to be 7 Å.<sup>1,2</sup> To transcend this limit, new gate dielectric materials must be developed to replace  $\text{SiO}_2$ . The 2005 edition of the *International Technology Roadmap for Semiconductors* anticipates the use of higher dielectric constant (high- $K$ ) gate dielectrics in production as early as 2007.<sup>3</sup> The first high- $K$  MOSFETs to enter the market will have gate dielectrics with  $K$  ranging between 10 and 20 and will later be replaced with materials having  $K$  greater than 20. One of these higher  $K$  candidate materials is  $\text{LaAlO}_3$ .<sup>3–6</sup>  $\text{LaAlO}_3$  is a promising high- $K$  gate dielectric due to its good thermal stability,<sup>7,8</sup> high optical band gap (5.6 eV for crystalline  $\text{LaAlO}_3$  and 6.2 eV for amorphous  $\text{LaAlO}_3$ ),<sup>9–11</sup> and high band offsets (1.8 eV for electrons and 3.2 eV for holes for amorphous  $\text{LaAlO}_3$ ).<sup>11</sup>

In crystalline form, the dielectric constant of  $\text{LaAlO}_3$  is  $24.1\pm0.1$  (measured at 145 GHz).<sup>12</sup> There is a significant discrepancy, however, in the literature for the dielectric constant of amorphous  $\text{LaAlO}_3$  thin films. Part of this discrepancy could be due to the films being off composition, as  $\alpha$ - $\text{Al}_2\text{O}_3$  has a  $K$  ranging from 9.4 to 11.6 as a function of direction.<sup>13</sup> If we restrict our consideration to only  $\text{La}_x\text{Al}_{1-x}\text{O}_3$  films with  $0.8\leq x\leq 1.2$ , the reported values vary from  $K=13$  to 27 depending on the deposition technique.  $\text{La}_{0.9}\text{Al}_{1.1}\text{O}_3$  films deposited by atomic layer deposition (ALD) have a reported  $K=13$ ,<sup>14</sup> sputtered  $\text{LaAlO}_3$  films have a  $K=14$ ,<sup>15</sup> electron-beam deposited  $\text{LaAlO}_3$  films have an estimated  $K=21$ –25,<sup>16,17</sup> metalorganic chemical vapor deposition deposited  $\text{La}_{0.8}\text{Al}_{1.2}\text{O}_3$  films have a  $K=25$ ,<sup>18,19</sup> and pulsed-laser deposited  $\text{La}_{1.04}\text{Al}_{0.96}\text{O}_3$  films have a  $K=25$ –27.<sup>20</sup>

In this letter, we report the dielectric properties of amorphous  $\text{LaAlO}_3$  thin films deposited on silicon by molecular-

beam deposition (MBD) using elemental lanthanum, aluminum, and  $\text{O}_2$  sources. The  $\text{LaAlO}_3$  thin films are stoichiometric and have no detectable interfacial layer between the  $\text{LaAlO}_3$  and the silicon.<sup>8,21</sup> The dielectric properties were extracted through capacitance-voltage ( $C$ - $V$ ) and current-voltage ( $I$ - $V$ ) characterization.

Amorphous  $\text{LaAlO}_3$  thin films (45, 60, and 75 Å thick) were grown by MBD in an EPI 930 MBD chamber modified for the growth of oxides.<sup>22</sup> The thickness of the films was determined from x-ray reflectivity (XRR) measurements using a Bede 300 mm system. The Bede REFS software was used to fit the XRR data. The films were grown on both  $n$ -type (phosphorous doped,  $0.2$ – $1\times 10^{15}$  P/cm<sup>3</sup>) and  $p$ -type (boron doped,  $1$ – $2\times 10^{19}$  B/cm<sup>3</sup>) Si (001) wafers. The silicon wafers were cleaned using a 50:1 solution of de-ionized (DI) water: concentrated hydrofluoric acid (HF). (The amorphous  $\text{LaAlO}_3$  films were formed by codepositing lanthanum, aluminum, and molecular oxygen at a background pressure of  $6\times 10^{-6}$  Torr onto unheated silicon wafers. The lanthanum and aluminum fluxes were each  $2\times 10^{13}$  atoms/cm<sup>2</sup> s. This deposition process has been shown to produce an abrupt amorphous  $\text{LaAlO}_3$ /Si interface free of any detectable interfacial  $\text{SiO}_2$ .<sup>8,21</sup> The films were capped *in situ* with a 1000-Å-thick aluminum film that served as the top electrode. The aluminum was patterned and wet etched using the Transene-type A aluminum etch<sup>23</sup> to produce  $50\text{ }\mu\text{m}\times 50\text{ }\mu\text{m}$  squares.

Several 1500-Å-thick amorphous  $\text{LaAlO}_3$  films have been analyzed by Rutherford backscattering spectrometry (RBS) (1.4 MeV  $\text{He}^+$ , 170° scattering angle). RBS indicates that the films are stoichiometric with a ratio of La:Al =  $1\pm 0.05$  (not shown).

The  $C$ - $V$  measurements were performed in a probe station using a HP 4284A. The electrical measurements were made on the as-deposited films and the results presented here are from  $C$ - $V$  measurements made on virgin devices. The  $I$ - $V$  measurements were made using a HP 4158A.

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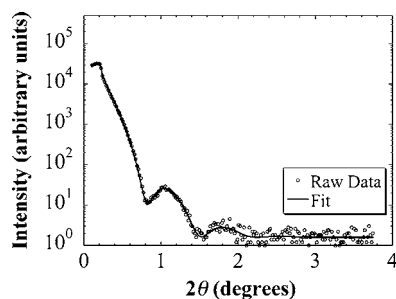


FIG. 1. X-ray reflectivity measurements and modeled data for an amorphous  $\text{LaAlO}_3$  film with a physical thickness of  $60 \pm 2$  Å.

The thickness of the  $\text{LaAlO}_3$  thin films was determined using XRR. Figure 1 shows the XRR measurement and the model for the  $60 \pm 2$  Å thin film. The physical thickness of the  $\text{LaAlO}_3$  thin films extracted by XRR is in agreement with high-resolution transmission electron microscopy measurements on similar films.<sup>21</sup>

Figure 2 shows the  $C$ - $V$  measurements of films deposited on  $n$ -type and  $p$ -type silicon, respectively. The equivalent oxide thickness (EOT) indicated in the figures was determined using the Hauser CVC modeling program.<sup>24</sup> The EOT values range between 9.8 and 15.5 Å for films deposited on  $n$ -type silicon with physical thicknesses of 45–75 Å. The EOT values range between 12.2 and 20.1 Å for films deposited on  $p$ -type silicon with physical thicknesses of 45–75 Å.

Figure 3 shows the  $I$ - $V$  measurements on  $n$ -type and  $p$ -type silicon, respectively, for the same films measured in Fig. 2. The leakage current densities are significantly lower for the films deposited on the  $n$ -type wafers and range between  $1 \times 10^{-3}$  and  $6 \times 10^{-7}$  A/cm<sup>2</sup> at  $V_{\text{fb}} + 1$  V for films with physical thicknesses of 45 and 75 Å. The leakage current densities for the films deposited on  $p$ -type wafers range

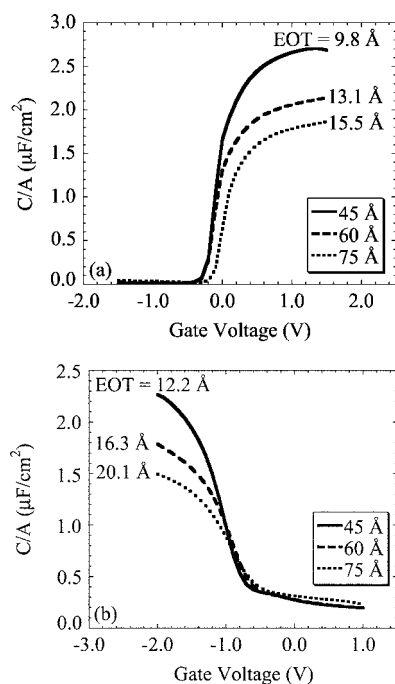


FIG. 2. (a)  $C$ - $V$  curves as a function of amorphous  $\text{LaAlO}_3$  film thickness on  $n$ -type wafers. (b)  $C$ - $V$  measurements as a function of thickness on  $p$ -type wafers. The measurements were made at 100 kHz on  $50 \mu\text{m} \times 50 \mu\text{m}$  capacitors.

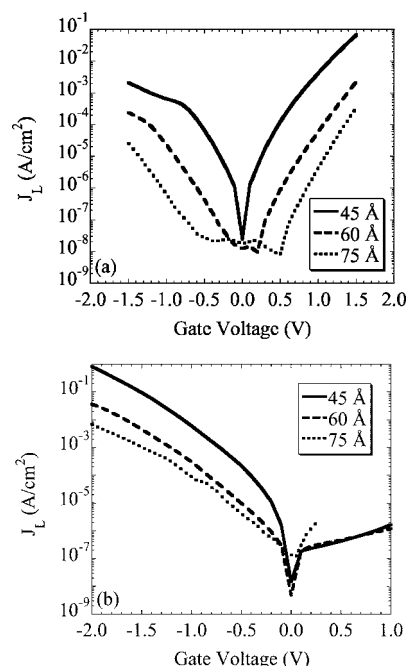


FIG. 3. (a)  $I$ - $V$  measurements as a function of amorphous  $\text{LaAlO}_3$  film thickness on the same  $n$ -type wafers shown in Fig. 2(a). (b)  $I$ - $V$  measurements as a function of thickness on the same  $p$ -type wafers shown in Fig. 2(b).

between  $0.8$  and  $8.5 \times 10^{-3}$  A/cm<sup>2</sup> at  $V_{\text{fb}} - 1$  V for films with physical thicknesses of 45–75 Å.

Figure 4 shows the forward and reverse bias sweeps for 45 Å  $\text{LaAlO}_3$  thin films deposited on  $n$ -type and  $p$ -type silicon, respectively. The  $n$ -type wafers showed significantly lower hysteresis than the  $p$ -type wafers. Several postdeposition anneals have also been performed to try to reduce the

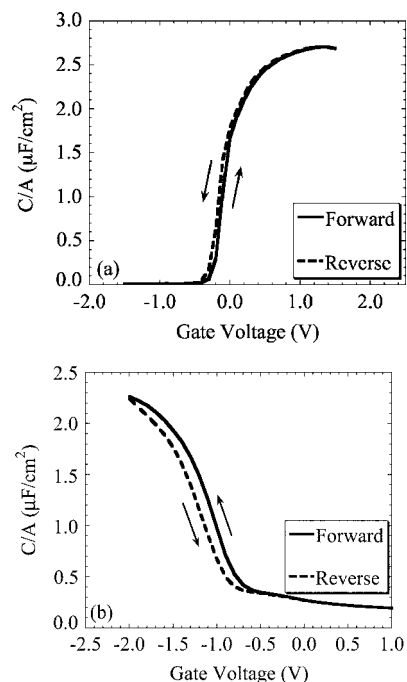


FIG. 4. (a) Forward and reverse bias  $C$ - $V$  measurements on a 45-Å-thick amorphous  $\text{LaAlO}_3$  thin film deposited on  $n$ -type silicon. The hysteresis was 66.1 mV. (b) Forward and reverse bias  $C$ - $V$  measurements on a 45-Å-thick amorphous  $\text{LaAlO}_3$  film deposited on  $p$ -type silicon. The hysteresis was 272 mV.

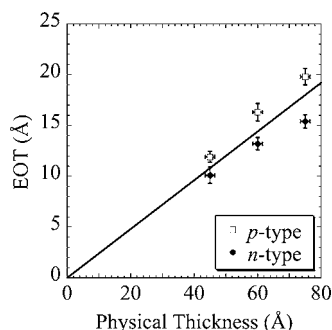


FIG. 5. EOT as a function of physical thickness for amorphous  $\text{LaAlO}_3$  films deposited on both  $n$ -type and  $p$ -type silicon.

hysteresis on  $p$ -type wafers. For example, samples annealed *in situ* in UHV directly after MBD at temperatures ranging between 400 and 600 °C for 30 min exhibited no improvement in the hysteresis. Subsequent *ex situ* annealing in forming gas (4% hydrogen and 96% nitrogen) at 350 °C for 30 min also did not improve the hysteresis of the  $\text{LaAlO}_3$  thin films deposited on  $p$ -type silicon. The as-deposited films were also *ex situ* annealed in  $\text{N}_2$  for 30 min at 750 °C, but this resulted in breaking down the films.

It was possible to eliminate the hysteresis by making multiple voltage sweeps on the same device. This indicates that there are traps in the  $\text{LaAlO}_3$  thin films deposited on  $p$ -type silicon. It is suspected that there might be a defect level in the band structure in the  $\text{LaAlO}_3$  near the valance band that causes the trapped states.

Figure 5 shows the EOT as a function of physical thickness for the films deposited on  $n$ -type and  $p$ -type silicon. The lack of a detectable interfacial layer<sup>21</sup> results in the intersection with the plot origin. From the slope of this plot, the dielectric constant of the amorphous  $\text{LaAlO}_3$  thin films deposited by MBD was extracted to be  $16 \pm 2$ . This dielectric constant is significantly lower than the dielectric constant of crystalline  $\text{LaAlO}_3$ , which is  $K=24$ .<sup>12</sup> The relatively low  $K$  value is, however, in good agreement with other  $\text{LaAlO}_3$  thin films deposited by ALD<sup>14</sup> and sputtering.<sup>15</sup>

Busani and Devine<sup>25</sup> proposed that the reduced dielectric constant of amorphous  $\text{LaAlO}_3$  thin films was caused by an increase in the molecular volume of the amorphous films that was caused by a lower density in sputtered amorphous  $\text{LaAlO}_3$  thin films compared to the density of single crystalline  $\text{LaAlO}_3$ . Using the thickness determined from XRR measurements and the areal density of cations deposited based on quartz crystal microbalance flux measurements calibrated by RBS measurements on thicker films, the density of our amorphous MBD  $\text{LaAlO}_3$  thin films was calculated to be  $4.3 \text{ g/cm}^3$ . This density is in good agreement with Busani and Devine's<sup>25</sup> sputtered  $\text{LaAlO}_3$  thin films and is significantly lower than the density of crystalline  $\text{LaAlO}_3$ , which is  $6.5 \text{ g/cm}^3$ . The dielectric constant of an isotropic and homogeneous amorphous material<sup>26</sup> (as well as certain cubic structures<sup>27</sup>) is related to its molecular volume by the Clausius–Mossotti equation<sup>28,29</sup>

$$K = \frac{3V_m + 8\pi\alpha_D^T}{3V_m - 4\pi\alpha_D^T}, \quad (1)$$

where  $V_m$  is the molar volume and  $\alpha_D^T$  is the total dielectric polarizability of the material.<sup>13</sup> Therefore, as the molecular

volume increases, the dielectric constant decreases. The increased molecular volume of our films resulting from their low density could be the reason for the reduced dielectric constant of amorphous  $\text{LaAlO}_3$  thin films deposited by MBD compared to crystalline  $\text{LaAlO}_3$ .

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